

ZnO NANOSTRUCTURES PREPARED BY RF SPUTTERING

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Summary ZnO is shortly reviewed as significant material for nanotechnology. Sputtered ZnO thin films showed columnar polycrystalline structure with preferred orientation in <002> direction, resistivity $\sim 1 \Omega\text{cm}$ and optical bandgap $E_g = 3,33 \text{ eV}$. Nanoclusters of Au and ZnO were formed by use of RF sputtering.

1. INTRODUCTION

Zinc oxide (ZnO) is a unique material that exhibits semiconducting, piezoelectric, and pyroelectric multiple properties which are a key phenomenon in building electro-/mechanical, optical, acoustic, thermal coupled sensors and actuators. Pure ZnO is colorless and crystallizes in the hexagonal (wurtzite) system with lattice parameters $a = 0,3296 \text{ nm}$ and $c = 0,52065 \text{ nm}$. The structure ZnO can be simply described by alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis (Fig 1) [1].

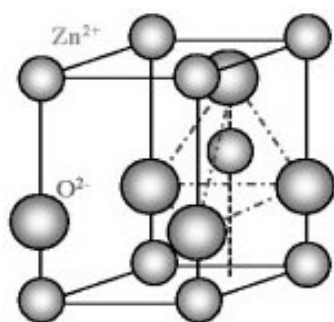


Fig. 1. Wurtzite structure model of ZnO with tetrahedral configuration

Zinc oxide is a transparent semiconductor with a direct bandgap of 3.37 eV and large excitation binding energy (60 meV), and exhibits near-UV emission and absorption, as well as high transparency and the natural n-type conductivity.

The semiconducting nanostructures such as nano-/fibers, wires, rods, tubes, belts, saws, springs, rings, bows and propellers (Fig. 2) have caught considerable attention due to zinc oxide great application potential in nanoactuators and nanosensors [2]. ZnO is bio-safe and bio-compatible, and can be used also for biomedical applications.

The highly one-dimensional ZnO nanostructures (wire, tubes, etc.) were realized using various methods such as vapor transport and deposition, thermal decomposition [3] and evaporation [4] (e.g. vapor liquid solid (VLS) process [6], metal-organic chemical vapor deposition (MOCVD) [7], metal-

organic vapor phase epitaxy (MOVPE) [8], growth by site-selective molecular beam epitaxy (MBE) [9].

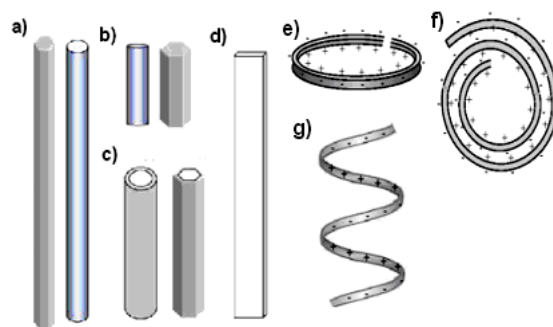


Fig. 2. Typical morphologies of one-dimensional nanostructures of ZnO a) nanowires/fibers, b) nanorod, c) nanotubes, d) nanobelts, e) nanoring, f) nanospiral, g) nanohelices [1, 5]

RF sputtering is capable: a low -temperature ion – assisted deposition of metals, semiconductors, insulators, the before/post deposition modification of substrate/thin - film surface by ions on the micro-/nano- level; change of deposition rate in wide range (0,1 to 10 nm/s); to control further parameters which are important for thin film growth (substrate temperature, plasma density, composition of working gas, ion bombardment of film during deposition).

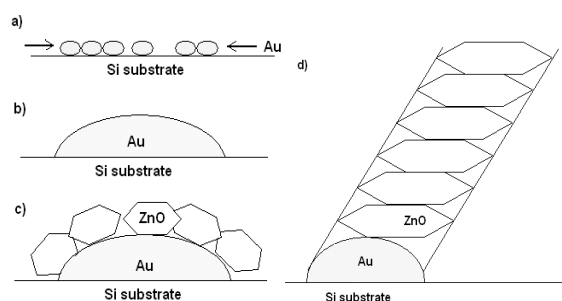


Fig. 3. Schematic illustration of nanostructure growth a) initial nucleation of Au atoms; b) formation of Au clusters; c) initial ZnO growth on the Au seeds; d) growth of ZnO nanofibers

In this work we report nanostructured surface on ZnO thin layer on silicon substrates using RF

sputtering technique with the use of gold as a catalyst. Therefore, it is key to be able to accurately control the position and size of the seeds Au particles during growth. For growth of nanostructures are dominant initial growth phases: seed formation, nucleation growth of clusters and islands, their coalescence. Schematic simplified growth of ZnO structures (nanodots, nanofibers) on Au particles is shown Fig 3.

2. EXPERIMENTAL PROCEDURE

The Au/ZnO structures were RF diode sputter deposited on Si and Corning glass substrates using a ZnO target (99.99 % purity, in 20 cm diameter) and metal Au target (99.95 % purity, in 20 cm diameter). The substrates were cleaned by standard chemical method. The sputtering chamber was pumped down to 10^{-5} Pa before admission of the sputtering gas Ar (99.9995 %) and total gas pressure 1,3 Pa was kept constant. The thickness of the ZnO thin film was 200 nm and the deposited Au thickness was approximately 10 nm ranges. The morphology of Au and ZnO structures were characterized using scanning electron microscope SEM LEO 1550. The crystal orientation and microstrains of the films were investigated by an automatic powder X-ray diffractometer AXS Bruker D8 with Eulerian cradle and 2D detector (CoK α , $\lambda = 0.179$ nm). The resistivity and carrier concentration in ZnO films were obtained from Van der Pauw measurements.

3. RESULT AND DISCUSSION

ZnO thin films were deposited by RF sputtering from the ZnO target in pure Ar gas. The resistivities of the of the sputter films was slightly dependent on the RF power, $\rho = 0,4 \div 1,0 \Omega\text{cm}$. The ZnO resistivity was determined by the carrier concentration which varied from $n = 1,4 \times 10^{19} \text{ cm}^{-3}$ to $n = 7 \times 10^{18} \text{ cm}^{-3}$. Transparency in VIS region was 85 %, with absorption edge in near UV region 3,33 eV which is close to the bandgap of bulk ZnO $E_g = 3.37$ eV.

The XRD diffraction lines of ZnO $\langle 100 \rangle$, $\langle 002 \rangle$ and $\langle 101 \rangle$, were observed (Fig 4.). The set of two-dimensional diffraction patterns of ZnO films deposited at Ar in sputtering gas displays three Debye rings of ZnO Bragg reflections (Fig. 5). The white circle is a Laue spot diffracted by substrate material (c-Si) due to the continuous X-ray radiation.

The morphologies of the deposited Au/ZnO structures are shown in Fig. 6 – Fig. 11. RF diode sputtered Au nanoparticles of mean diameter of 10^{th} nm (Fig. 6) were as seeds for growth of nanostructured surface of ZnO thin films in thickness of 200 nm (Fig. 10).

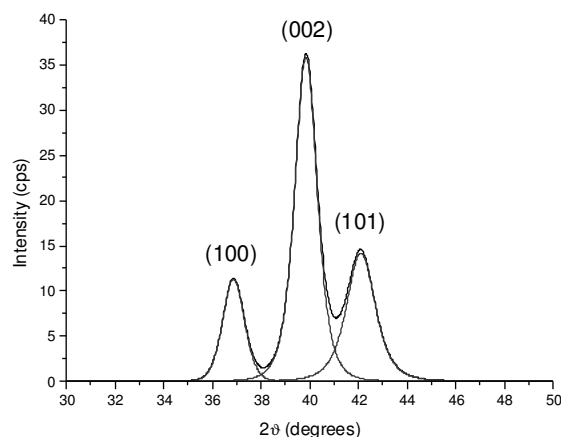


Fig 4. Two dimensional diffraction pattern of ZnO film



Fig 5. Sputtered ZnO thin films showed columnar polycrystalline structure with preferred orientation in $\langle 002 \rangle$ direction

All substrates were bombarded by Ar ions before deposition Au to increase the cleanness and micro roughness. Fig. 6 shows Au surface after to the high rate deposition at the temperature of 300°C . This caused an increase of roughness and decrease of reflexion. The clusters have an average linear dimension of $1 \mu\text{m}$.

In comparison with that, the sample of the same Au thickness prepared at room temperature exhibits sparkle a surface with smaller seeds (Fig. 7). Fig. 8 shows Au-coated Si substrate by lower deposition rate and after deposition in annealed vacuum at temperature of 300°C . The Au formed separate seeds with diameters of 10 - 40nm. The size of seeds became more homogenous when we used two - step deposition. In the first step we deposited Au film with the rate of $0,8 \text{ nm/s}$ and thickness of 250 nm. In the second step we used low deposition rate ($0,3 \text{ nm/s}$) and amount of Au corresponding to thickness of 50 nm. Substrate temperatures were 300°C during deposition and after deposition substrate was annealed in vacuum (150°C) (Fig 9). Au-seeds on Si Corning glass substrates were used as base for forming of ZnO nano - crystalline structures by RF sputtering (Fig. 10 and Fig 11).

Linear size of these nanostructures were lower or equal to 100 nm.

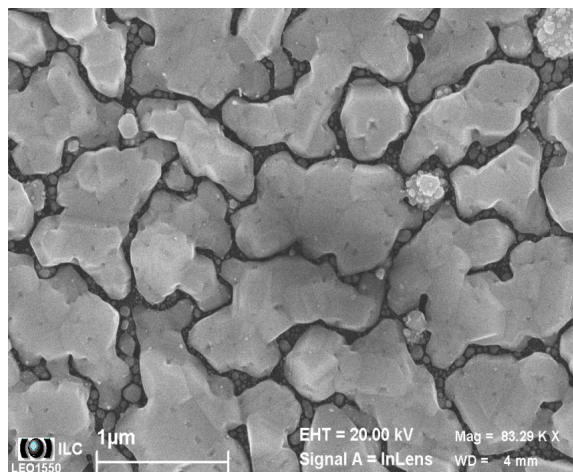


Fig. 6. Au on the Si substrates, the Au rate deposition 0,8 nm/s at temperature $t = 300^{\circ}\text{C}$.

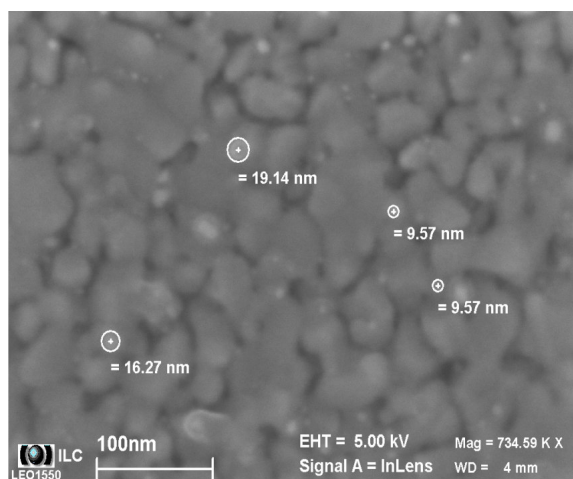


Fig. 7. Au on the Si substrates, the Au rate deposition 0,8 nm/s at temperature $t = 23^{\circ}\text{C}$.

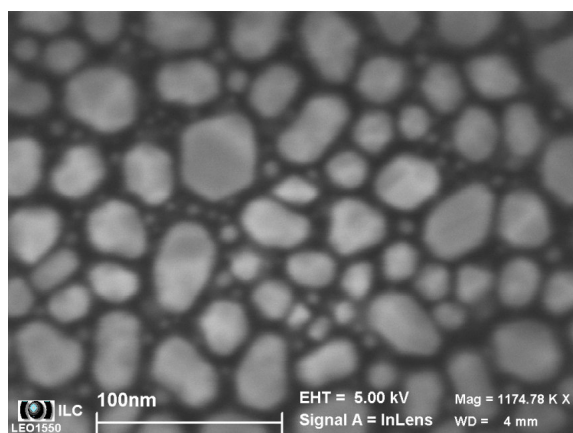


Fig. 8. Au on the Si substrates, the Au rate deposition 0,3 nm/s at temperature $t = 300^{\circ}\text{C}$, annealing in vacuum at $t = 300^{\circ}\text{C}$.

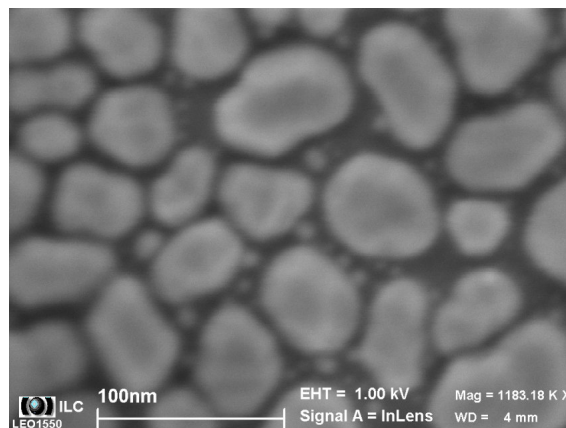


Fig. 9. Au on the Si substrates, the Au rate deposition 0,8 nm/s and 0,3 nm/s at temperature $t = 23^{\circ}\text{C}$, annealing in vacuum at $t = 150^{\circ}\text{C}$.

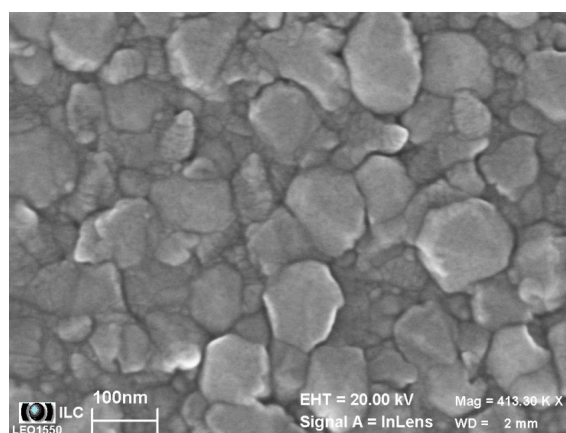


Fig. 10. Nanostructured surface of ZnO thin film on the Si substrate.

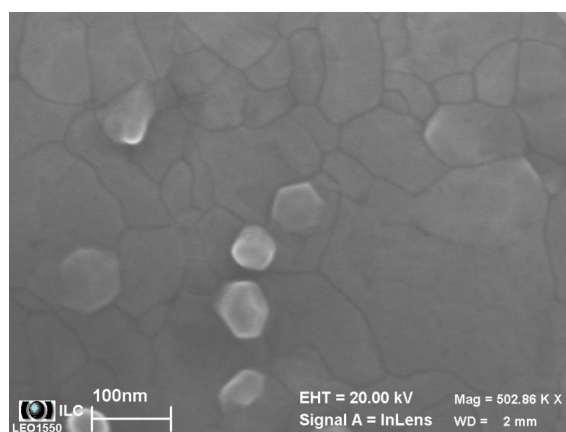


Fig. 11. Nanostructured surface of ZnO thin film on the Corning glass substrate

4. CONCLUSIONS

ZnO offers the broad spectrum of unique physical and chemical properties, what is getting it into group of the most important nanomaterials for integration with microsystems and biotechnology. Our preliminary results have confirmed that

sputtering is one of available deposition method for forming of chosen ZnO nanostructures. Future target is to use of nanostructured surface of ZnO thin films for modern DNA-based biosensors.

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REFERENCES

- [1] Wang, Z. L., Kong, X. Y.: *Adv. Funct. Mater.*, October (2004), 14, No. 10, 943
- [2] Choopun, S., et al.: *Journal of Crystal growth* 282 (2005) 365
- [3] Xu, C. K., Xu. G. D., Liu. Y. K., Wang, G.H.: *2002 Solid State Commun.* 122, 175
- [4] Yao, B.D., Chan, Y. F., Wang, N.: *Appl. Phys., 2002 Lett.* 81,1287
- [5] Ding, Y., Wang, Z. L.: *J. Phys. Chem. B*, Vol. 108, No. 33, 2004, 12280
- [6] Hsu, H.C., et al : *Nanotechnology* 16 (2005) 297
- [7] Muthukumar et col.: *IEEE transctions on nanotechnology*, Vol 2, NO 1. March 200, 50
- [8] Liu, C., Zapien, J.A., Yao, Y. , Meng, X. , Lee, C.S., Fan, S., Lifshitz, Y., Lee, S.T.: *Adv. Mater.* 15 (2003) 838.
- [9] Heo et al: *Appl. Phys. Lett.*, Vol. 85, No. 15, 11 October 2004, 3107